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A test method for halogenated hydrocarbons has been evaluated and information is provided for the user. Four compounds were investigated, methylene chloride, methyl chloroform, Freon 113 and ethylene dibromide. Cylinder gases used for calibration and auditing were tested for stability. Decreases in concentration of 3-4% per month were observed. Tedlar and aluminized Mylar containers were also tested. Tedlar bags were found to be superior, maintaining Freon 113 samples stable for 10 days, methyl chloroform for 7 days, methylene chloride for 6 days and ethylene dibromide for 2 days, at room temperature. Heating caused decreases in stabilities. Heated ethylene dibromide samples were more stable in aluminized Mylar than in Tedlar. A procedure was developed to remove persistent residues from Tedlar bags that had contacted high concentrations of halogenated hydrocarbons. Information is also included on gas chromatographic columns for use in this method of analysis.

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EVALUATION OF EMISSION TEST METHODS FOR HALOGENATED HYDROCARBONS VOLUME II: CH_2Cl_2, CH_3CCl_3, $CF_2ClCFCl_2$, AND CH_2BrCH_2Br

by

Joseph E. Knoll, Mark A. Smith, and M. Rodney Midgett
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

The following investigation was conducted at the request of the Office of Air Quality Planning and Standards. A test method for the measurement of halogenated hydrocarbon emissions from stationary sources was evaluated. The work included a study of integrated bag sampling techniques and methods of gas chromatographic measurement. Some information was also obtained on the stability of halogenated hydrocarbons in compressed gas mixtures. Volume I of this series dealt with carbon tetrachloride, ethylene dichloride, tetrachloroethylene, and trichloroethylene. In the present study, the applicability of this test method for the analysis of ethylene dibromide, Freon 113, methyl chloroform, and methylene chloride was evaluated.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ABSTRACT

The techniques used in a source test method for halogenated hydrocarbons were evaluated. Cylinder gases used for calibration and auditing were tested for stability. Decreases in concentration of 3-4% per month were observed for Freon 113, methyl chloroform, and methylene chloride. Tedlar and aluminized Mylar bags used in integrated sampling were also studied. In general, Tedlar bags were found to be superior, maintaining Freon 113 samples stable for 10 days, methyl chloroform for 7 days, methylene chloride for 6 days and ethylene dibromide for 2 days, at room temperature. Heated ethylene dibromide samples, however, were more stable in aluminized Mylar than in Tedlar. The chromatographic column specified in the test method was also evaluated. It resolved all of the compounds of interest, with the exception of ethylene dibromide. A suitable column is recommended for that substance.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

°C	-- degree Celsius
EPA	-- U.S. Environmental Protection Agency
ft	-- foot
hr	-- hour
i.d.	-- inside diameter
in	-- inch
µl	-- microliter
ml	-- milliliter
min	-- minute
OAQPS	-- Office of Air Quality Planning and Standards
o.d.	-- outside diameter
ppm	-- part per million

SYMBOLS

CH_2Cl_2	-- methylene chloride
CH_3CCl_3	-- methyl chloroform
$CF_2ClCFCl_2$	-- Freon 113
CH_2BrCH_2Br	-- ethylene dibromide
N_2	-- nitrogen

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SECTION 1

INTRODUCTION

Volume I of this series reported on the evaluation of source test methods for carbon tetrachloride, ethylene dichloride, tetrachloroethylene, and trichloroethylene (1). These substances have been selected by the U.S. Environmental Protection Agency (EPA) as compounds for which human exposure must be limited (2). The source test method under consideration, EPA tentative Method 23, was formulated in the Emission Measurement Branch, Emission Standard and Engineering Division, Office of Air Quality Planning and Standards (OAQPS) (see Appendix A).

The present study was undertaken to evaluate the applicability of Method 23 for the analysis of methylene chloride (CH_2Cl_2), methyl chloroform (CH_3CCl_3), Freon 113 ($CF_2ClCFCl_2$), and ethylene dibromide (CH_2BrCH_2Br). The first three of these compounds are employed as industrial solvents, while the fourth is an important chemical intermediate. The tentative method under consideration employs Tedlar or aluminized Mylar bags for sample collection and gas chromatography with flame ionization detection for analysis. The use of bottled gas mixtures is one calibration option.

Every sampling method should employ a container that preserves the sample free from contamination and change. Tedlar bags have been successfully employed for this purpose in the source sampling methods for vinyl chloride (3) and for benzene (4). Recent work on the use of plastic containers for source sampling methods are reviewed in Volume I of this study (1). The present investigation was carried out to obtain information on the stability of gas mixtures containing CH_2Cl_2, CH_3CCl_3, $CF_2ClCFCl_2$, and CH_2BrCH_2Br in Tedlar and aluminized Mylar bags. Some information was also obtained on the efficacy of

compressed gas mixtures for use as secondary standards during field measurements as well as on chromatographic columns for resolution of the compounds of interest.

The work for this study was carried out in the Source Branch of the Quality Assurance Division, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina; this laboratory has a program to evaluate and standardize source emission test methodology.

SECTION 2

CONCLUSIONS

Aluminum cylinders containing CH_3CCl_3, CH_2Cl_2, and $CF_2ClCFCl_2$ in nitrogen (N_2) decrease in concentration by 3-4% per month over a period of 4 months.

Tedlar bags can be used to store samples of CH_3CCl_3 in N_2 at source-level concentrations for at least 7 days with a decrease in concentration of less than 10%. Tedlar bag samples of $CF_2ClCFCl_2$ remain stable for at least 10 days, CH_2Cl_2 for at least 6 days, and CH_2BrCH_2Br for less than 2 days.

When stored in aluminized Mylar bags, samples of CH_2Cl_2 in N_2 remain stable for 4 days, CH_3CCl_3 for 2 days, $CF_2ClCFCl_2$ for 11 days, and CH_2BrCH_2Br for 2 days.

Tedlar bag samples of CH_3CCl_3 in air are as stable as samples in N_2. Heating to 75°C for 16 hrs causes no change in the concentration of CH_3CCl_3 samples stored in Tedlar bags. The same schedule of heating causes $CF_2ClCFCl_2$ and CH_2Cl_2 gas samples to decrease in concentrations by 45 and 17%, respectively.

Aluminized Mylar bag samples of $CF_2ClCFCl_2$ remain stable when heated to 75°C for 16 hours, while samples of CH_3CCl_3 decrease in concentration by 20%.

Residues formed in Tedlar bags due to their exposure to high concentrations of CH_2Cl_2 and $CF_2ClCFCl_2$ can be removed through a procedure of flushing three times with N_2, heating for one hour at 60°C, and then flushing again. Residues of CH_3CCl_3; however, cannot be removed in this manner.

The chromatographic column specified in EPA Method 23 (20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport in 15-ft X 1/8-in stainless steel)

is capable of resolving CH_2Cl_2, CH_3CCl_3, and $CF_2ClCFCl_2$, but not CH_2BrCH_2Br. The latter compound may be resolved using a column consisting of 1,2,3-tris-(2-cyanoethoxy)propane on 80/100 mesh Chromasorb P AW in 6-ft x 1/8-in stainless steel.

SECTION 3

EXPERIMENTAL

Tedlar bags were fabricated from 2-mil plastic sheets. The edges were sealed with a Vertrod Thermal Impulse Heat Sealing Machine (Model 48 EPS 1/4 WC). Connections to the bag were made using an O-Seal Straight Thread Adapter with 0.25-in o.d. tube and a 7/16-20 thread (Swagelok 401-A-OR) which was inserted through a 2-in square piece of VisQueen polyethylene tape fixed to the outside surface of the bag. The adapter was held in place with a 0.058-in Teflon washer (0.5 in i.d. x 1-in o.d.) and a 7/16-20 nut. A 7115G4B Hoke ball valve was connected to the adapter. The Tedlar bags had a volume of approximately 100 liters. Aluminized Mylar bags were obtained from Calibrated Instruments, Inc., (Ardsley, NY). These bags had a volume of 6 liters and were fitted with a hose connection to which it was necessary to adapt the Hoke valve by means of a section of Tygon tubing. In making this connection, the length of Tygon tubing was minimized in order to reduce the contact between the gas and the Tygon plastic.

Cylinders containing gaseous mixtures of N_2 and the halogenated hydrocarbons under investigation were obtained from Airco, Inc. (Research Triangle Park, NC). Hydrocarbon concentrations were determined using calibration standards prepared in Tedlar bags. These were made by injection of the liquid compound while filling the bags with N_2. The N_2 was measured using a No. 802 Singer dry gas meter; a No. 801, 10-µl Hamilton syringe was used to measure the compounds of interest. In other instances, Tedlar bags were filled directly from the reference cylinders.

Halogenated hydrocarbon concentrations were determined using a Hewlett-Packard Model 5930A gas chromatograph equipped with dual flame ionization detectors and a 0.1-ml sampling loop. A Hewlett-Packard Model 18850A integrating terminal was employed to record output. The chromatographic

column consisted of a 15-ft x 1/8-in stainless steel helix packed with 20% SP-2100/0.1% Carbowax 1500 on 100/200-mesh Supelcoport. The following operating conditions were employed: inlet temperature, 250°C; column, 75°C; detector, 300°C; carrier gas, liquid air N_2 at 20 ml/min. Under these conditions, only a single peak could be observed in each compound of interest. The bags were sampled by drawing the gas through the chromatographic sampling loop using a vacuum pump. Bottled gases were forced through the sampling system under their own impetus. A benzene and a toluene gas mixture were used to normalize the gas chromatograph results.

In several instances, gas samples containing high concentrations of the subject compounds were introduced into Tedlar bags. These atmospheres were prepared by slowly passing N_2 gas through an impinger containing the liquid compound under study. The concentration was calculated for the saturation vapor pressure of the halogenated hydrocarbon at 0°C, the temperature at which the impinger was maintained. This temperature was chosen to assure that condensation would not take place in the bag during the subsequent study.

Retention indices were determined for several halogenated hydrocarbons and a number of other selected compounds on five chromatographic columns. The columns were:

- Carbopak C-HT, 80/100 mesh in 6.5-ft x 1/8-in stainless steel
- 10% FFAP on 80/100 mesh acid-washed Chromasorb W in 20-ft x 1/8-in stainless steel
- TCEP (1,2,3-tris(2-cyanoethoxy)propane on 80/100 mesh Chromasorb P AW, 6-ft x 1/8-in stainless steel
- 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport in 15-ft x 1/8-in stainless steel
- 15% tetracyanoethylated pentaerythritol on 60/80 mesh Chromasorb P AW in 16-ft x 1/8-in stainless steel

The columns were obtained from Supelco, Inc. (Belefonte, PA) and were conditioned overnight at a temperature and flow rate recommended by the manufacturer. The compounds under investigation were used without further purification.

Relative retentions in Kovats retention index units (5) were obtained from chromatograms of suitable mixtures containing n-alkanes as internal standards. Retention distances measured between point of injection and peak maxima were corrected for the column gas holdup volume by means of retention of methane (6). The adjusted retentions were then used to calculate values for the retention index by means of the expression recommended by the Chromatography Discussion Group (7):

$$I = 100\ N + 100\ n \frac{\log R_X - \log R_N}{\log R_{N+n} - \log R_N}$$

where R_X, R_N, and R_{N+n} are the adjusted retentions of the solute and n-alkanes containing N and N+n carbon atoms, respectively.

SECTION 4

RESULTS AND DISCUSSION

STABILITY OF HALOGENATED HYDROCARBON GAS MIXTURES IN ALUMINUM CYLINDERS

Because cylinder gases were used as calibration standards for our studies, and also because of plans to use such cylinders in future quality assurance programs, a study was undertaken to determine if compressed gas mixtures containing the chlorinated hydrocarbons under investigation remained stable in cylinders. A single aluminum cylinder each of CH_3CCl_3, CH_2Cl_2, and $CF_2ClCFCl_2$ were employed. In each case, the diluent gas was N_2. The gases were measured at various intervals over a period of approximately 4 months. The results are listed in Table 1.

A stability test was carried out by performing a linear regression analysis on each set of data and fitting it to the following equation:

$$Y = A + BX$$

where Y corresponds to concentration in ppm, X to time in days and A and B are constants. To determine whether the slope, B, was significantly different from zero, a "t-test" was performed. This consisted in determining a calculated t-value:

$$t_c = (B - \beta)/S_b$$

where β is a hypothesized slope of zero and S_b is the standard error of the slope. The quantity t_c was then compared with tabulated t-values for the appropriate number of degrees of freedom and the 0.95 level of confidence (8). Each of the three data sets in Table 1 show values for the ratio t_c/t_t greater than unity, indicating that a slope of zero can be rejected with confidence.

The rates of change for the subject gases in Table 1 of from 3-4% per month is too small to detect until after several months have passed. However, the analysis given above is evidence that these decays are real. Therefore, when cylinders of such gases are used for calibration purposes, they should be reanalyzed after several months to determine if their concentrations have changed.

STABILITY OF HALOGENATED HYDROCARBON SAMPLES IN TEDLAR AND ALUMINIZED MYLAR BAGS AT AMBIENT TEMPERATURES

The stability of samples of CH_3CCl_3, CH_2Cl_2, CH_2BrCH_2Br and $CF_2ClCFCl_2$ in Tedlar and aluminized Mylar bags was studied. Several bag samples of each compound were prepared by either filling the bags directly from standard cylinders or by injecting measured amounts of liquid into bags filled with known volumes of either N_2 or air. The bags were measured over a period of days on a Hewlett-Packard 5830 gas chromatograph and concentrations were determined by comparison with measurements of standard cylinders.

The results of these measurements are listed in Tables 2 through 6. For each series of data, a first order decay constant, k, was calculated along with the quantity, $t_{0.9}$, an estimate of the time required for the sample to decay to 90% of its initial value. This latter quantity was determined as representative of the useful storage time of a sample. First order decay constants were determined to compare the decay rates of the different series of data using a simple curvilinear function. Actually, there is no evidence that the decay processes under study were in fact first order.

The results in Table 2 show that CH_3CCl_3 has excellent stability in Tedlar. One sample of approximately 10 ppm had a $t_{0.9}$ of 7 days while bag samples in the 60-200 ppm range had $t_{0.9}$ values of 25 days or greater. A bag made using air gave the same results as those using N_2. In contrast, the results in Table 6 showed CH_3CCl_3 to be unstable in an aluminized Mylar bag, which had a $t_{0.9}$ of less than 2 days.

Methylene chloride showed good stability in Tedlar and fair stability in an aluminized Mylar bag. The decay rate in Tedlar was relatively independent of concentration in the 30-200 ppm range. The storage time ($t_{0.9}$) was at least 10 days in Tedlar and 4 days in aluminized Mylar (Tables 3 and 6).

Freon 113 displayed good stability in both Tedlar and aluminized Mylar (Tables 4 and 6). In considering this data, it should be noted that all the concentrations studied were in the 10-20 ppm range where such good stability is not always observed. At higher concentrations even better stability might be expected. One bag had a storage time of 6 days, while the others were nearly twice that. Based on these results, a permissible storage time of at least 6 days would be indicated for $CF_2ClCFCl_2$ in Tedlar and in aluminized Mylar.

In contrast, the compound CH_2BrCH_2Br is unstable in both Tedlar and aluminized Mylar. The data in Tables 5 and 6 indicate that such CH_2BrCH_2Br samples decay to approximately 90% of their initial values in approximately 2 days. The nature of this decay is illustrated in Figure 1, which contains a plot of the data in Table 5. First order decay lines have been fitted through the points, and it is evident that the removal of this brominated compound continues with time and does not reach a steady state value, making storage of this compound risky. Consequently, the analysis of such samples would best be carried out within a few hours of sample collection.

These results of the stability of halogenated hydrocarbons in aluminized Mylar and Tedlar bags may be used to evaluate the maximum length of time a sample may be retained, prior to analysis. In making such judgments, consideration should be given to the concentration range in question and to the fact that the aluminized Mylar bags were smaller than the Tedlar bags used in this study. Smaller bags, having a greater surface to volume ratio, provide a relatively greater degree of contact between the gaseous components and the surface, and probably result in more rapid decay. Accordingly, the stability tests using aluminized Mylar bags were more stringent than those carried out in Tedlar.

STABILITY OF HALOGENATED HYDROCARBON SAMPLES IN TEDLAR AND ALUMINIZED MYLAR BAGS AT TEMPERATURES ABOVE AMBIENT

The bag stability study reported above was carried out in a 20-25°C temperature range. However, source emissions often take place at considerably higher temperatures; samples collected from such heated streams may expect to remain above the 20-25°C range for a considerable time. For this reason, a study was made of the stability of halogenated hydrocarbon gas mixtures in aluminized Mylar and in Tedlar bags at temperatures above ambient. The temperature range selected was from 70-75°C. This range was selected because it is sufficiently high to show the effects of heating on concentration stability, without damaging the container. Volume I of this investigation reported the effects on concentration of temperature both above and below ambient (1). Since at temperatures below ambient there were no observable changes in concentration, the effects of temperatures below ambient were not considered in the present study. However, the procedures followed were the same as those described in Volume I. The bags were heated for the required time period and then brought to room temperature for measurement.

One result of the heating was to cause the release of some residual materials from the plastics. However, the amounts released were small compared with the concentrations under consideration in this study. Another result was that the seals on several of the aluminized Mylar bags opened up when heated to 70°C, this in spite of the fact that the temperature range had been chosen to minimize such damage. The results in Table 7 show that CH_3CCl_3 gas mixtures were stable in Tedlar bags for 19 hrs at 70°C, but underwent a decrease in an aluminized Mylar bag at that temperature. In contrast, $CF_2ClCFCl_2$ displayed the opposite behavior — stable in aluminized Mylar but unstable in Tedlar. Methylene chloride underwent a 17% decrease after being heated to 75°C for 16 hours.

Certain conclusions can be drawn from these results. Heating of aluminized Mylar bags should be avoided unless absolutely necessary. One exception is in the collection of $CF_2ClCFCl_2$ from heated sources. Tedlar is

a better choice for CH_3CCl_3. Samples of CH_2Cl_2 in Tedlar bags may be exposed to temperatures of 75°C for a few hours without significant loss.

MEMORY EFFECTS RESULTING FROM HIGH CONCENTRATIONS

A study was made of "memory" effects caused by the exposure of Tedlar bags to very high concentrations of halogenated hydrocarbons. The amount of residues resulting in bags subjected to high concentrations of the halogenated compounds of interest was measured and procedures to remove them were evaluated.

To carry out this study, a high concentration gas sample was prepared for each compound and introduced into a new Tedlar bag. After standing at room temperature for 1 hr, the bag was flushed by evacuating it and filling it with N_2 three times. After the flushing, the concentration of the bag was measured. The bag was then heated for 1 hr at 60°C and the concentration was remeasured. After repeating the entire procedure, the bag was again measured. In one case, the flushing and heating procedure was carried out a third time. The results of the measurements are listed in Table 8.

Each bag contained residues of the compounds which were not removed by flushing. Heating caused the release of additional materials which had been absorbed by the plastic. The bags were considered to be decontaminated satisfactorily when the concentration produced after heating was less than 1 ppm.

The results of this study show that Tedlar bags exposed to high concentrations of CH_2Cl_2 and $CF_2ClCFCl_2$ can be decontaminated through a procedure of flushing with N_2, heating for 1 hr, then flushing again. Residues of CH_3CCl_3, however, cannot be removed in this manner.

SEPARATION OF HALOGENATED HYDROCARBONS BY GAS CHROMATOGRAPHY

Volume I of this investigation reported on the separation of halogenated hydrocarbons by gas chromatography. It discussed the chemical nature of five columns in common use and listed tables of retention indices. Such tables are often used as a guide in selecting chromatographic columns for separating complex mixtures and for making preliminary identifications of components.

In the present study, Kovats retention indices were also measured for the four compounds of interest. However, in place of the Porapak T column reported on in Volume I, a column containing a stationary phase consisting of 1,2,3-tris(cyanoethoxy)propane was substituted in the present study. The results are listed in Table 9. In employing this information in the discussion below, comparisons have been made with the retention indices tabulated in Volume I.

The column specified in the Tentative Method (SP-1200) resolves CH_2Cl_2 and $CF_2ClCFCl_2$ well and elutes them before most of the gasoline hydrocarbons, and from many other halogenated hydrocarbons. The SP-2100 column also resolves CH_3CCl_3 well but elutes it in the middle of the gasoline spectrum. Therefore, it would be difficult to resolve this compound on SP-2100 if gasoline vapor were present. Ethylene dibromide is not resolved on the SP-2100 column. (It is strongly retained and elutes as a broad peak at high temperatures.)

Carbopak C-HT elutes CH_2Cl_2, $CF_2ClCFCl_2$, and CH_3CCl_3 well before the gasoline hydrocarbons. This column would appear to be very useful for determining low molecular weight halogenated hydrocarbons when gasoline hydrocarbons are present. However, on this column $CHCl_3$ and CCl_4 interfere with the analysis of $CF_2ClCFCCl_2$ and CH_3CCl_3, respectively, and CH_2BrCH_2Br is not resolved.

The columns designated FFAP and TCP (see Table 9) appear to offer few advantages over the two columns that were discussed above for determining the four compounds of interest. Neither resolves CH_2BrCH_2Br. Although on TCP, many halogenated hydrocarbons elute well beyond the gasoline region, $CF_2ClCFCl_2$ does not.

Retention indices of the four compounds of interest are also included for the column designated TCEP (see Table 9). It was employed in this investigation because of its ability to resove CH_2BrCH_2Br. A column employing TCEP is used in the Tentative Method for the Determination of Benzene from Stationary Sources (4), where it has been shown to be a practical column for field measurements.

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TABLE 1. TIME VARIATION OF CONCENTRATIONS OF HALOGENATED HYDROCARBONS IN ALUMINUM CYLINDERS

Elapsed Time, days	Concentration, ppm		
	$CF_2ClCFCl_2$	CH_2Cl_2	CH_3CCl_3
0	14.3	-	-
1	-	41.0	15.0
12	13.7	40.3	14.7
13	14.0	-	-
20	13.2	38.9	14.2
26	14.1	41.6	15.2
35	13.1	38.7	14.1
43	13.6	39.9	14.2
50	13.3	39.1	14.2
62	13.6	39.7	14.4
68	13.3	38.1	14.0
77	12.6	36.4	13.5
119	11.8	34.1	13.1
120	11.3	32.7	12.8
Slope, %/month	-3.67	-4.01	-3.07
Standard Deviation, %/month	0.70	0.55	0.63
Degrees of Freedom	11	10	10
t_c/t_t*	2.92	4.02	2.69

*Calculated t-value/Tabulated t-value

TABLE 2. VARIATION OF CH_3CCl_3 CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	CH_3CCl_3 Concentration, ppm				
	Bag 1	Bag 2	Bag 3	Bag 4	Bag 5†
0	13.5	213	104	60.0	61.0
1	-	-	-	55.1	55.2
3	12.8	209	102	-	-
4	-	-	-	64.0	59.8
6	12.4	206	101	62.1	60.7
7	12.5	208	102	-	-
8	-	-	-	62.0	57.2
10	11.4	199	98	-	-
11	-	-	-	59.6	61.9
12	-	-	-	57.4	59.6
14	11.1	202	100	-	-
17	10.4	197	97	-	-
k, $days^{-1}$	-.015	-.004	-.004	0	0
$t_{0.9}$, days	7.0	25	29	**	**

*From date when bags were prepared.

†Bag 5 contained CH_3CCl_3 in air. Bags 1-4 contained CH_3CCl_3 in N_2.

**Indicates no evidence that decay took place.

TABLE 3. VARIATION OF CH_2Cl_2 CONCENTRATION OF GAS MIXTURE STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	CH_2Cl_2 Concentration, ppm		
	Bag 1	Bag 2	Bag 3
0	39.8	183	48.4
1	-	182	48.0
4	37.8	-	-
5	38.2	176	46.7
6	-	176	47.0
7	37.9	-	-
8	-	173	46.8
11	35.6	-	-
12	-	160	43.8
13	35.5	-	-
14	-	160	43.6
k, $days^{-1}$	-0.01	-0.01	-0.008
$t_{0.9}$, days	10.5	10.2	13.9

*From date when bags were prepared.

TABLE 4. VARIATION OF $CF_2ClCFCl_2$ CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	$CF_2ClCFCl_2$ Concentration, ppm		
	Bag 1	Bag 2	Bag 3
0	11.8	17.5	20.0
12	10.2	15.0	17.3
13	10.8	13.3	18.2
k, $days^{-1}$	-0.009	-0.02	-0.009
$t_{0.9}$, days	12	6	11

*From date when bags were prepared.

TABLE 5. VARIATION OF CH_2BrCH_2Br CONCENTRATION OF GAS MIXTURES STORED IN TEDLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	CH_2BrCH_2Br Concentration, ppm	
	Bag 1	Bag 2
0	20.0	11.4
2	17.3	10.1
4	16.1	8.7
5	14.7	8.1
18	8.1	3.7
19	7.5	3.6
k, $days^{-1}$	-0.05	-0.06
$t_{0.9}$, days	2.1	1.7

*From date when bags were prepared.

TABLE 6. VARIATION OF HALOGENATED HYDROCARBON CONCENTRATIONS OF GAS MIXTURES STORED IN ALUMINIZED MYLAR BAGS AT AMBIENT TEMPERATURES

Elapsed Time, days*	Halogenated Hydrocarbon Concentration, ppm			
	CH_2Cl_2	CH_3CCl_3	$CF_2ClCFCl_2$	CH_2BrCH_2Br
0	20.0	12.0	13.3	17.3
1	19.5	10.5	12.6	13.9
2	17.8	-	-	-
4	-	9.2	12.8	12.9
5	17.6	9.0	12.4	13.1
k, $days^{-1}$	-0.026	-0.06	-0.009	-0.05
$t_{0.9}$, days	4.1	1.9	11	2.2

*From date when bags were prepared.

TABLE 7. EFFECT OF TEMPERATURE ON HALOGENATED HYDROCARBON CONCENTRATION OF GAS MIXTURES STORED IN ALUMINIZED MYLAR AND TEDLAR BAGS

Compound	Bag Type	Temperature (°C)	Time, (hr)	Concentration, ppm		Change (%)
				Initial	Final	
CH_3CCl_3	Al-mylar	75	16	13.2	10.3	-22
"	Tedlar	70	1	197	196	-0.5
"	Tedlar	70	19	196	188	-4
$CF_2ClCFCl_2$	Al-mylar	75	16	11.7	11.5	-2
"	Tedlar	70	1	9.93	10.1	+2
"	Tedlar	70	16	18.4	10.1	-45
CH_2Cl_2	Tedlar	75	1	160	165	+3
"	Tedlar	75	16	165	137	-17

TABLE 8. "MEMORY" EFFECTS IN TEDLAR BAGS RESULTING FROM HIGH CONCENTRATIONS OF HALOGENATED HYDROCARBONS

Compound	Concentration, ppm				
	Initial*	After flushing	After heating	After second heating**	After third heating
CH_3CCl_3	48,300	72.6	105	4.3	4.5
CH_2Cl_2	179,900	4.0	107	0.9	-
$CF_2ClCFCl_2$	142,300	0.6	1.1	0.5	-

*Calculated from vapor pressure at 0°C.

**Bag flushed before second and third heatings.

TABLE 9. KOVATS RETENTION INDICES OF SELECTED HALOGENATED HYDROCARBONS ON VARIOUS CHROMATOGRAPHIC COLUMNS

Compound	Retention index				
	SP-2100	FFAP	TCP	C-HT	TCEP
CH_2Cl_2	516	934	1001	362	1073
$CF_2ClCFCl_2$	524	695	602	440	639
CH_3CCl_3	646	900	980	490	911
$CH_2ClCHCl_2$	753	1447	1172	565	-
CH_2BrCH_2Br	-	-	-	-	1575
CH_3CH_2Br	514	-	882	-	-

SP-2100: 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport 15-ft x 1/8-in stainless steel.

FFAP: Free fatty acid Carbowax 20M reacted with nitroterephathalic acid (10%) on 80/100 mesh Chromasorb W AW in 20-ft x 1/8-in stainless steel.

TCP: 15% Tetracyanoethylated pentaerythritol on 60/80 mesh Chromasorb P AW in 16-ft x1/8-in stainless steel.

C-HT: Carbopak C-HT, 80/100 mesh in 6.5-ft x 1/8-in stainless steel.

TCEP: 10% 1,2,3-tris(2-cyanoethoxy)propane on 80/100 mesh Chromasorb P AW in 6-ft x 1/8-in stainless steel.

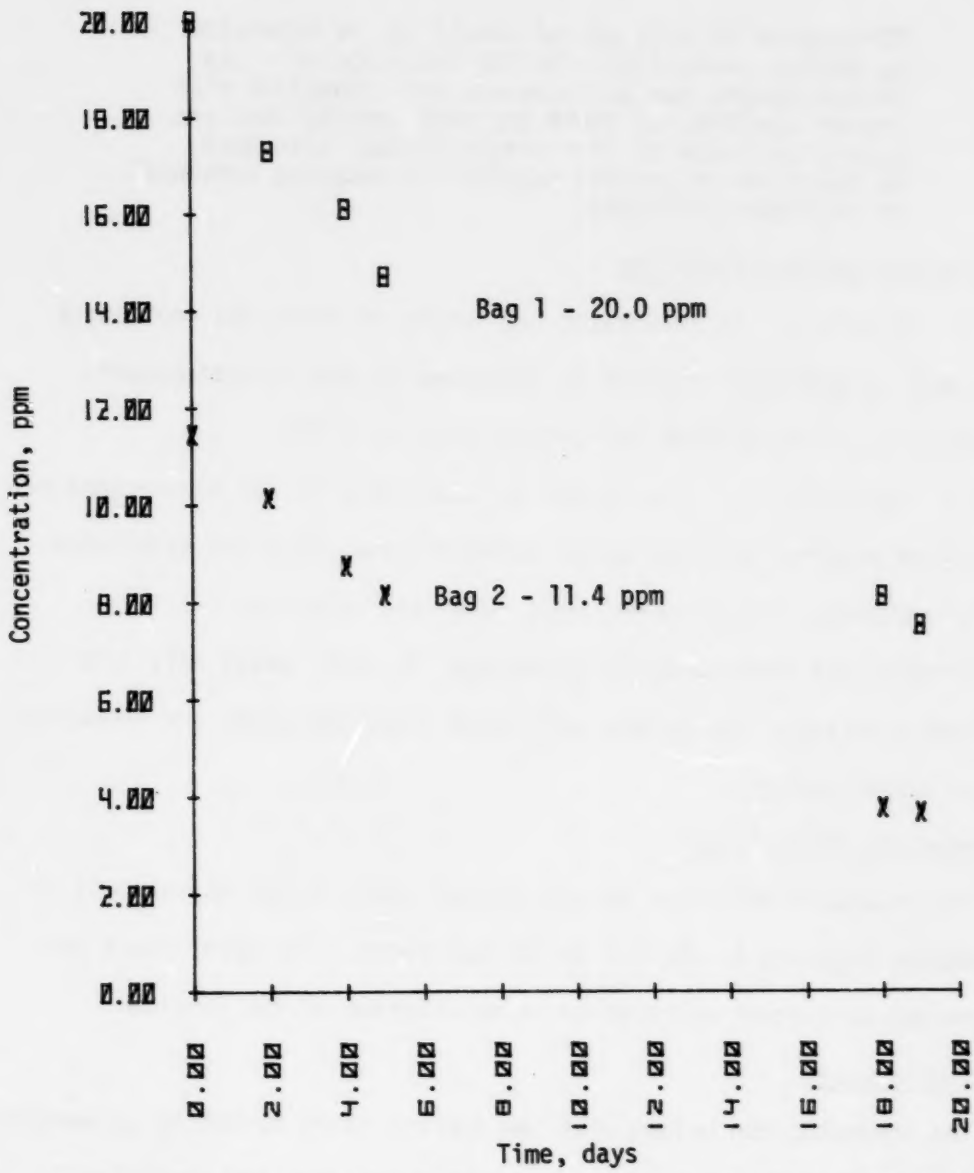


Figure 1. Decay of ethylene bromide stored in Tedlar bags at ambient temperature.

APPENDIX A

METHOD FOR THE DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

METHOD 23. DETERMINATION OF HALOGENATED

ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. Principle and Applicability

1.1 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

1.2 Applicability. The method is applicable to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1-1-1 trichloroethane, and trichlorotrifluoroethane in stack gases only from specified processes. It is not applicable where the gases are contained in particulate matter.

2. Range and Sensitivity

The procedure described herein is applicable to the measurement of halogenated organics in the 0.1 to 200 ppm range. The upper limit may be extended by further calibration or by dilution of the sample.

3. Interferences

The chromatograph column with the corresponding operating parameters herein described has been represented as being useful for producing adequate resolution of halogenated organics. However, resolution

interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of the particular compound of interest without reducing the response to that compound, as specified in Section 4.3.1.

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator. Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or G.C./mass spectroscopy, is available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 23-1).

4.1.1 Probe. Stainless steel, Pyrex[1] glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter if particulate matter is present.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure 23-1.

4.1.4 Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

[1]Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-Free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal Tube. To prevent admission of halogenated organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 23-1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm of the halogenated organic compound that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Column. Stainless steel, 3.05 m x 3.2 mm, containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. Other columns can be used, provided that the precision and accuracy of the analysis of standards are not impaired. Information confirming that adequate resolution of the halogenated organic compound

peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromotographic Peak Resolution."

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 25 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.4 Syringe. 50 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.5 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize solvent.

5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Halogenated organic compound, 99 mol percent pure, certified by the manufacturer to contain a minimum of 99 mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen) for which the gas composition has been certified with an accuracy of ±3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration

does not change by greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified concentration of the halogenated organic compound and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.2.2.

5.2.3.1 Cylinder Standards Certification. The concentration of the halogenated organic compound in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 200 and 400 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 50 and 100 ppm) for verification of the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low concentration standard exceeds 5 percent of the true concentration, determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by

one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1.1 and using 99 mol percent of the halogenated organic compounds, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards, if such analysis is available. All calibration standards must be reverified on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards identical in preparation to those in Section 5.2.3 (the halogenated organic compounds of interest, in nitrogen), except the concentrations are only known to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low concentration cylinder in the range of 25 to 50 ppm, and one high concentration cylinder in the range of 200 to 300 ppm. When available, audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternate source must be secured.

6. Procedure

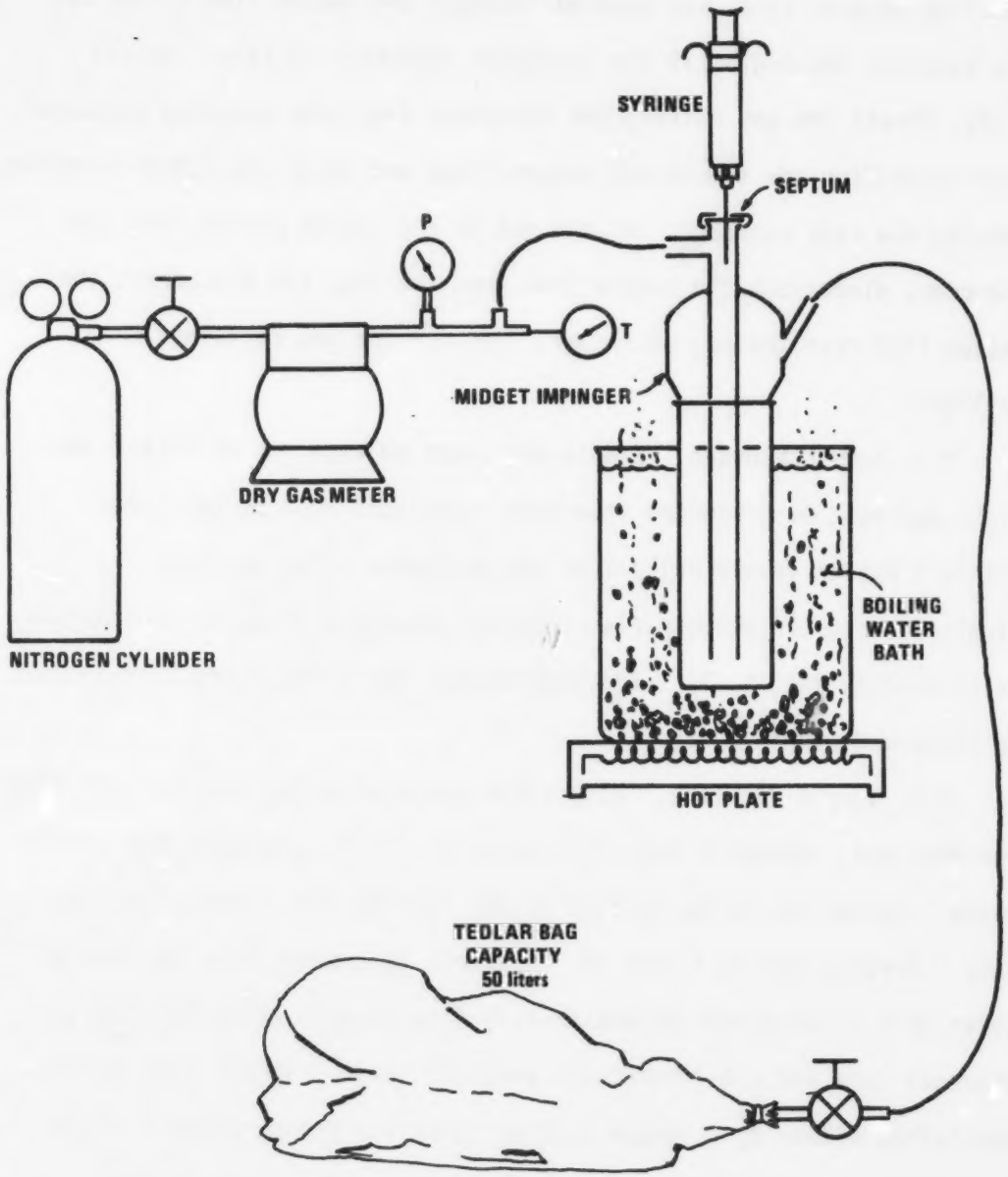
6.1 Sampling. Assemble the sample train as in Figure 23-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the

centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

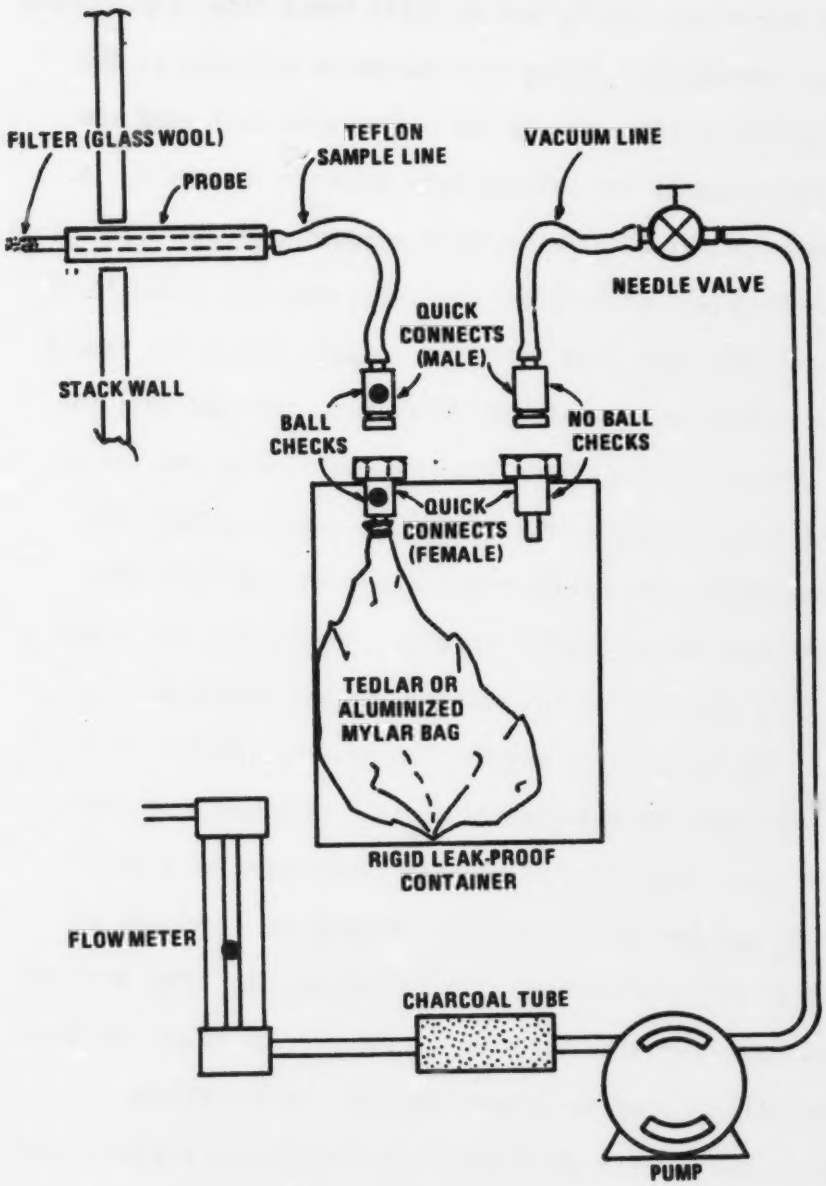
6.2 Sample Storage. Sample bags must be kept out of direct sunlight and must be protected from heat. Analysis must be performed within 1 day of sample collection for methylene chloride, ethylene dichloride and trichlorotrifluoroethane. Analysis of perchloroethylene, trichloroehtylene, 1, 1, 1-trichloroethane and carbon tetrachloride must be performed within 2 days.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0-100 ml/min rotameter with flow control valve followed by a charcoal tube and a 0-1 inch w.g. pressure gauge. Sample flow may be maintained either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

TRAIN FOR PREPARATION OF SAMPLES



INTEGRATED - BAG SAMPLING TRAIN



6.4 Analysis. Set the column temperature to 100° C, and the detector temperature to 225° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to the halogenated organic compound as determined in Section 7.2.1. Measure the halogenated organic compound peak area, A_m, by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Standards, Calibration, and Quality Assurance

7.1 Standards.

7.1.1 Preparation of Standard Gas Mixtures. (Optional-delete if cylinder standards are used.) Assemble the apparatus shown in Figure 232. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. Refer to Table 23-1. While the bag is filling, use the 50 μl syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200 ppm. In a like manner, use the 25 μl syringe to prepare bags having approximately 100 and 50 ppm concentrations. To calculate the specific concentrations, refer to Section 8.1. Tedlar bag gas mixture standards of methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for 1 day; trichloroethylene and 1, 1,1-trichloroethene for 2 days; perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Halogenated Organic Compound Retention Time. This section can be performed simultaneously with Section 7.2.2. Establish chromatograph conditions identical with those in Section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the

TABLE 23-1. INJECTION VALUES FOR PREPARATION OF STANDARDS. (Optional, see Section 7.1.1)

Compound	Molecular Weight (M)	Density at 293° A (D)	µl Liquid Required in 50 l N_2 for Approximate Concentration of: 200 ppm	100 ppm	50 ppm
Perchloroethylene C_2Cl_4	165.85	1.6230	42.5	21.2	10.6
Trichloroethylene C_2HCl_3	131.40	1.4649	37.3	18.6	9.3
1,1,1-Trichloroethane $C_2H_3Cl_3$	133.42	1.4384	38.6	19.3	9.6
Methylene Chloride CH_2Cl_2	84.94	1.3255	26.6	13.3	6.7
Trichlorotrifluoroethane $C_2Cl_3F_3$	187.38	1.5790	49.3	24.7	12.3
Carbon Tetrachloride CCl_4	153.84	1.5940	40.1	20.1	10.0
Ethylene Dichloride $C_2H_4Cl_2$	98.96	1.2569	32.7	16.4	8.2

injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 6.3), flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the halogenated organic compound peak retention time. Since it is possible that there will be other organics present in the sample, it is very important that positive identification of the halogenated organic compound peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c, the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two

values versus C_c. When ther other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Optional Standards Concentrations. Calculate each halogenated organic standard concentration prepared in accordance with Section 7.1.1 as follows:

$$C_c = \frac{B\mu l \ \frac{D\ \mu g}{\mu l} \ \frac{10^3\ \mu g}{mg} \ \frac{\mu g\ mole}{M\ \mu g} \ \frac{24.055\ \mu l}{\mu g\ mole} \ 10^6}{V_m\ Y\ \frac{10^6\ \mu l}{l} \ \frac{293}{T_m} \ \frac{P_m}{760}}$$

$$= \frac{\frac{BD}{M}\ (24.055 \times 10^3)}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 23-1}$$

Where:

C_c = Standard concentration in ppm.

B = Number of µl of injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

D = Density of compound at 293° A.

M = Molecular weight of compound.

24.055= Ideal gas at 293° A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of C_c that corresponds to A_c. Calculate C_s as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r\ (1-S_{wb})} \qquad \text{Equation 23-2}$$

Where:

S_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of the halogenated organic in the sample in ppm.

C_c = The concentration of the halogenated organic indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

9. References

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4. Communication From Joseph E. Knoll. Test Method for Halogenated Hydrocarbons. December 20, 1978.